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In re Application of:	)	
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Ya XU et al.	)	Confirmation No. 7133
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Application No.: 10/516,617	)	Group Art Unit: 1794
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Filed: August 29, 2005	)	Examiner: Gray, Jill M.
	)	
For: EXTREMELY FINE SHAPE MEMORY ALLOY WIRE, COMPOSITE MATERIAL THEREOF AND PROCESS FOR PRODUCING THE SAME	)	**Mail Stop Amendment**

Mail Stop Amendment
Commissioner of Patents
U.S. Patent and Trademark Office
Alexandria, VA 22314

Madam:

SUBMISSION OF VERIFIED TRANSLATION

Applicants submit herewith a Verified Translation of Japanese Patent Application No. 2002-162287 filed in Japan on June 4, 2002.

Applicants do not believe that any fees are required with this paper and respectfully request that this Translation be made of record in this application.

EXCEPT for issue fees payable under 37 C.F.R. § 1.18, the Commissioner is hereby authorized by this paper to charge any additional fees during the entire pendency of this application including fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment to Deposit Account No. 50-0310.

Respectfully submitted,

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STATEMENT

I, Satoshi OGUSHI—of 7-13, Nishi-Shimbashi 1-chome, Minato-ku, Tokyo 105-8408 Japan —hereby declare that I am conversant in both Japanese and English and that I believe the following is a true and correct translation of a specification of Japanese Patent Application No.2002-162287.

Date: January 5, 2009

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JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: June 4, 2002

Application Number: Japanese Patent Application No. 2002-162287

[JP 2002-162287]

Applicant(s): NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY

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Commissioner, Japan Patent Office Yasuo Imai (sealed)

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[List of Submitted Article]

[Name of Article] Specification 1

[Name of Article] Drwaings 1

[Name of Article] Abstract 1

[Necessity of Proof] Necessary

[Designation of Document] Specification

[Title of the Invention] FUNCTIONAL COMPOSITE MATERIAL USING EXTREMELY FINE SHAPE MEMORY ALLOY WIRE AND PROCESS FOR PRODUCING THE SAME

[Claims]

[Claim 1] A functional composite material molded by hardening a shape memory alloy wire in a martensitic phase with a resin matrix material, in which the shape memory alloy wire is prepared by using a shape memory alloy which assumes an austenitic phase or a martensitic phase through phase transformation temperatures and subjecting to a cold drawing work, wherein an extremely fine shape memory alloy wire is used as the shape memory alloy wire.

[Claim 2] The functional composite material according to claim 1, wherein the extremely fine shape memory alloy wire has a diameter of 0.06 mm or less and a cold drawing rate of at least 20% or more and in a martensitic phase.

[Claim 3] The functional composite material according to claim 1 or 2, wherein one or two or more kinds of a glass fiber and carbon fiber is used in combination other than the shape memory alloy wire.

[Claim 4] The functional composite material according to any one of claims 1 to 3, wherein the resin matrix material is thermoset-molded at a temperature of 180°C or less.

[Claim 5] The functional composite material according to any one of claims 1 to 4, wherein the shape memory alloy is a Ti-Ni alloy.

[Claim 6] The functional composite material according to any one claims 1 to 5, wherein the shape memory alloy wire is heated to a reverse transformation termination temperature (Af) or more to cause a martensitic reverse transformation and change a martensitic phase to an austenitic phase to generate a shrinking power.

[Claim 7] The functional composite material according to claim 6 which generates the shrinking power, wherein the shape memory alloy wire heated is a part of the whole of the shape memory alloy wire.

[Claim 8] A process for producing a functional composite material using a shape memory alloy wire, which is molded by embedding the shape memory alloy wire subjected to a cold drawing work in a resin matrix material at a phase transformation termination temperature or less.

[Claim 9] A process for producing the functional composite material according to claim 6 or 7, wherein an electric current is applied to a part or whole of the shape memory alloy wire in an embedded cold working state for a short time to heat to a phase transformation temperature or more, and after causing a reverse transformation the electric current is turned off to cause a small influence of heat on the surrounding resin matrix material.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention pertains]

The present invention relates to a process for producing a functional composite material using an extremely fine shape memory alloy wire.

More specifically, the invention relates to a process for producing a functional composite material using a shape memory alloy, wherein a pre-strain of a shape memory alloy wire is generated by subjecting the shape memory alloy to a cold work in a martensitic phase state to form an extremely fine wire, and since a reverse transformation temperature is elevated by the cold work, when the shape memory alloy wire is embedded in a matrix material resin such as an epoxy resin which is thermoset-molded at 180°C to form a composite, an apparatus and a control for retaining the pre-strain of the shape memory alloy wire are not necessary.

[0002]

[Background Art]

It has been confirmed that a pre-strained shape memory alloy wires are embedded in a CFRP, a GFRP, Al or the like to exhibit a vibration-controlling function and a retarded fatigue crack-developing rate. These utilize an effect that an elongation strain imparted beforehand in a low temperature martensitic phase state remains after only

removal of the stress and that they are reverse-transformed into a mother phase by heating after molding so that they can restore the original shapes. In 2001, we have developed a functional composite material using a shape memory alloy, wherein the reverse transformation temperature of a TiNi wire having a diameter of 0.4 mm is elevated to the curing temperature or more of a matrix material such as an epoxy resin which is molded at 130°C by a cold work treatment, thereby the TiNi wire can be easily embedded without causing any reverse transformation and any shrinkage of the TiNi wire during curing molding at 130°C even when the TiNi wire is not fixed at the both ends, and a process for producing the same. However, the present technique can be applied to only functional composite materials which cure and mold at 130°C. The present technique cannot be applied to heat-resistant CFRP and GFRP to be molded at 180°C, which are the most important in aviation and space industries.

[0003]

[Problems to be solved by the Invention]

In the invention, by dissolving the above defect and using the extremely fine shape memory alloy wire subjected to a cold work, it could be achieved that the effect of the cold work was sufficiently produced, the reverse transformation temperature was elevated more, and the larger pre-strain was obtained compared to the pre-

strain of the conventional thick wire subjected to a cold work. Because of this, it has been developed a functional composite material in which a TiNi wire keeping a shrinking strain of 2% or more on hold during curing molding at 180°C can be embedded even when the TiNi wire is not fixed at the both ends. It has also been developed a process for producing the same. Moreover, by using the extremely fine shape memory alloy wire, it can be handled same as a carbon fiber. Therefore, a production of a pre-impregnation material comprising the extremely fine shape memory alloy wire becomes possible. In addition, an efficiency of the mold work can be improved and a quality thereof can be stabilized, and then it has a big meaning for practical applications of the functional composite material using the shape memory alloy.

Moreover, by heating the embedded TiNi wire by application of electric current for a short time, the reverse transformation temperature of the TiNi wire returns to normal one, and a process for producing the functional composite material able to utilize the shape-memory effect of the TiNi wire.

Moreover, in the cold work treatment, only a wiredrawing treatment during the wire production step is utilized to generate a shrinking strain and to control the reverse transformation temperature, thereby it is expected that a production cost can be considerably reduced. In

addition, since a yield stress of the TiNi wire is largely increased in a martensitic phase state by the cold work, it provides a functional composite material using the shape memory alloy in which the effect of the strength at a low temperature and increase of stiffness are expected, and a process for producing the same.

[0004]

[Means for Solving the Problems]

In this invention, in the shape memory alloy which assumes an austenitic phase or a martensitic phase through phase transformation temperatures, the reverse transformation temperature is elevated by the cold work treatment. However, the phenomena are known that when reverse-transformed, the reverse transformation temperature returns to normal one (the temperature reverse-transformed).

The present inventors have found a surprising fact that the reverse transformation temperature range and given pre-strain are increased more by subjecting the extremely fine shape memory alloy wire to a cold drawing work, and further found that even when the reverse transformation temperature is set to 180°C which is a practical level, the shape memory alloy able to utilize the shrinking strain still sufficiently can be obtained. Thereby, by using the shape memory alloy, the functional composite material and

the process for producing the same of the invention was achieved.

As a typical embodiment, by subjecting to a cold work in which a cold drawing work rate is 20% or more, preferably about 35% in a martensitic phase, a pre-strain of a TiNi shape memory alloy wire having a final diameter of 0.06 mm or less was generated. In addition, by this cold drawing work, the reverse transformation temperature was elevated and this TiNi wire was embedded in a matrix material such as a CFRP, a GFRP, an epoxy resin or the like which are cured at temperatures up to 180°C.

It is revealed that the functional composite material can be produced by using the shape memory alloy having a shrinking strain increased up to 3.5% and the above matrix material.

In addition, when this functional composite material was molded, an apparatus and control for holding the pre-strain of the TiNi shape memory alloy wire was not necessary.

[0005]

Fig. 1 shows a measured result of a shrinking strain of a Ti-50 at% Ni alloy having a diameter of 0.05 mm with a cold drawing rate of 35%. For comparison, it also shows a measured result of a shrinking strain of a Ti-50 at% Ni sample having a diameter of 0.4 mm with a cold drawing rate of 35%. The following is revealed. With

regard to the wire having a diameter of 0.05 mm, in the case of the first heating, the shrinking strain is 3.5%, the reverse transformation temperature As is 133°C, and the reverse transformation temperature Af is 267°C. On the other hand, with regard to the wire having a diameter of 0.4 mm, in the case of the first heating, the shrinking strain is 2.3%, the reverse transformation temperature As is 130°C, and the reverse transformation temperature Af is 210°C. From the above results, in the case of the extremely fine wire, at the same cold work amount of 35%, it is revealed that the shrinking strain increases to 3.5% and the reverse transformation temperature range becomes very broad and shifts to a high-temperature side.

In addition, in the second heating, in the case of the extremely fine wire, the reverse transformation temperature As becomes 29°C, Af becomes 67°C, and thus the reverse transformation temperature range returned to the same level as in the case of a sample without being subjected to the cold work.

Furthermore, a change of the shrinking strain involved in reverse transformation was investigated by measuring thermal expansion on the extremely fine wires after thermal treatment at 130°C and 180°C each for 2 hours. The results are shown in Figs. 2 and 3, respectively. In the wire thermally treated at 130°C for 2 hours, it is revealed that the shrinking strain becomes

about 3.0% and the reverse transformation temperature range increases largely and becomes in the range of 160 to 264°C.

In addition, in the wire thermally treated at 180°C for 2 hours, it is revealed that the shrinking strain becomes about 2.5% and the reverse transformation temperature range increases largely and becomes in the range of 197 to 271°C. From the results, after curing molding the composite material at 180°C, a shrinking strain of 2.5% still remains in the extremely fine wire subjected to this cold work. Thereby, it is considered that a restoring stress of 250 MPa or more is obtained.

[0006]

[Mode for Carrying Out the Invention]

Based on such research results, the functional composite material and the process for producing the same of the invention were conceived. The invention is explained by specifically showing the process for producing the functional composite material using the extremely fine TiNi wire subjected to a cold work treatment.

The invention provides a method for obtaining a shape-restoring power by heating the extremely fine TiNi wire by application of electric current in the embedded cold work state.

There are problems that the reverse transformation temperature is not returned to normal ones and the restoring power is hardly utilized unless the wire which is

embedded in the matrix material and restrained is reverse-transformed.

However, it is necessary to heat up to the reverse transformation termination temperature (in the case of the cold work rate of 35%, it is about 270°C) in order to be reverse-transformed the sample which has undergone cold work. Since this temperature exceeds the curing temperature of the matrix material, there is a possibility that the characteristics of the matrix material receive an adverse effect when heating.

At this point, by utilizing that the reverse transformation is an endothermic reaction, the particular heating process was developed.

Specifically, the embedded TiNi wire is once heated for a very short time with high current to cause the reverse transformation, and then the current was immediately turned off. Since the reverse transformation is an endothermic reaction and the current is turned off before elevating the temperature in the vicinity of the surface of the wire, the influence of the heat on the surrounding matrix material is small.

Thereby, the reverse transformation temperature of the TiNi wire returns to the normal one, and the restoring power can be obtained by heating with low current.

[0007]

The shape memory alloy for use in the invention is typically TiNi, but any shape memory alloy may be used as long as the shape memory alloy is a shape memory alloy having a diameter of 0.06 mm or less which assumes an austenitic phase or a martensitic phase through phase transformation temperatures.

[0008]

In the invention, by subjecting to an appropriate cold work treatment, the reverse transformation temperature of the extremely fine TiNi wire is elevated to a curing temperature or more of the matrix material such as a CFRP, a GFRP, an epoxy resin or the like, and it becomes possible that the TiNi wire is embedded during curing at 180°C even when the TiNi wire is not fixed at the both ends. Furthermore, by heating the embedded TiNi wire by application of electric current for a short time, the reverse transformation temperature of the TiNi wire returned to the normal one, and then the functional composite material able to utilize the shape memory effect of the TiNi wire could be produced.

In addition, in the cold work treatment, since only the wiredrawing treatment during the wire production step is utilized to generate a pre-strain and to control the reverse transformation temperature, it is expected that a production cost is largely reduced.

In addition, the resin matrix material for use in the invention is typically an epoxy resin, but other thermosetting resins such as a phenol resin and a polyamide resin may be used. As long as the strength can be retained, a thermoplastic resin may be used in combination.

[0009]

[Examples]

Examples of the invention are specifically described.

A Ti-50 at% Ni wire (diameter: 0.05 mm) having a cold drawing rate of 35% was kept at 180°C for 2 hours and embedded in a CFRP (carbon fiber reinforced plastic) to prepare a functional composite material having damage-suppressing and vibration-controlling functions.

Since the molding conditions for this CFRP were at 180°C for 2 hours, the cold-worked wire was kept at 130°C for 2 hours and then, the shrinking strain and change of the reverse transformation temperature range were measured.

Fig. 3 shows the result. Form this, it was revealed that the cold-worked wire retained a shrinking strain of 2.5% even when thermally trated at 180°C for 2 hours. As it is already found from the aforementioned result, it is considered that a restoring stress of 250 MPa or more is obtained by this shrinking strain of 2.5%.

[0010]

Fig. 4 shows a cross-section of the TiNi/CFRP composite material prepared by embedding a wire having a diameter of 0.05 mm, which is observed by SEM. Fig. 4(a) shows one in the case of an angle of 90° between the wire and the carbon fiber, and Fig. 4(b) shows one in the case that the wire is embedded in the layer of an angel of 0 to 90° of the carbon fiber.

[0011]

Fig. 5 shows experimental results on a crack-suppressing effect detected when the wire embedded is heated by application of electric current with respect to the composite material manufactured. Fig. 5(a) shows a change of shrinking strain of the sample surface when an electric current is applied, and Fig. 5(b) shows a temperature change of the sample surface when an electric current is applied.

[0012]

[Advantage of the Invention]

By employing the above mechanism, the invention allows that, without using both fixing apparatus for retaining pre-strain of the shape memory alloy, the reverse transformation temperature and pre-strain is controlled by the cold work and heating treatment by application of electric current and the functional composite material able to utilize the stable restored power of the shape memory alloy is thermoset-molded at 180°C. Furthermore, in the

invention, since the extremely fine shape memory wire having a diameter of 0.06 mm or less is used, and with regard to the pre-strain of the shape memory wire, only the wiredrawing treatment during the wire production step is used, it can be handled same as a carbon fiber, and thereby the production of the pre-impregnation material comprising the extremely fine shape memory alloy wire becomes possible. In addition, efficiency of the molding work is improved and the quality thereof is stabilized and the production cost can be largely reduced, thereby practical applications of the functional composite material using the shape memory alloy have a big meaning.

[Brief Description of the Drawings]

[Fig. 1] It is a drawing showing measured results of a shrinking strain change involved in reverse transformation of a Ti-50 at% Ni wire with a cold work rate of 35% by heat expansion measurement. (a) shows results in the case of wire having a diameter of 0.05 mm, and (b) shows results in the case of wire having a diameter of 0.4 mm.

[Fig. 2] It is a drawing showing measured results of a shrinking strain change involved in reverse transformation of a Ti-50 at% Ni wire (diameter of 0.05 mm) which is subjected to thermal treatment at 130°C for 2 hours and has a cold work rate of 35%.

[Fig. 3] It is a drawing showing measured results of a shrinking strain change involved in reverse transformation

of a Ti-50 at% Ni wire (diameter of 0.05 mm) which is subjected to thermal treatment at 180°C for 2 hours and has a cold work rate of 35%.

[Fig. 4] It is a cross-section of a TiNi/CFRP composite material prepared by embedding wire having a diameter of 0.05 mm, which is observed by SEM. Fig. 4(a) shows one in the case of an angle of 90° between the wire and the carbon fiber, and Fig. 4(b) shows one in the case that the wire is embedded in the layer of an angel of 0 to 90° of the carbon fiber.

[Fig. 5] It is experimental results on a crack-suppressing effect detected when the wire embedded is heated by application of electric current with respect to the composite material manufactured. Fig. 5(a) shows a change of shrinking strain of the sample surface when an electric current is applied, and Fig. 5(b) shows a temperature change of the sample surface when an electric current is applied.

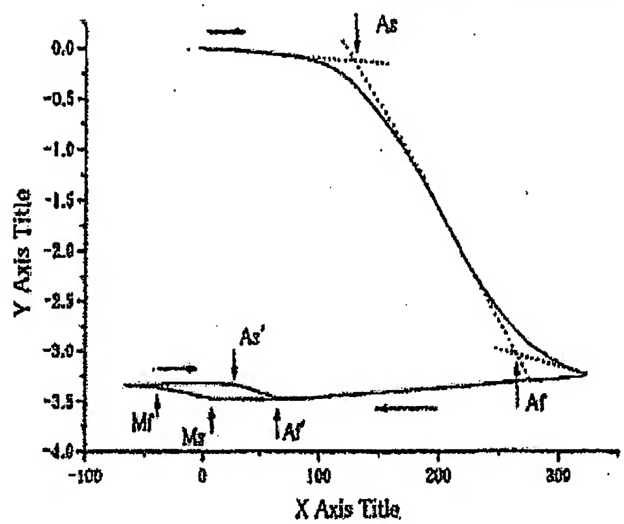
[Description of the Drawings]

1. As: reverse transformation starting temperature
2. Af: reverse transformation termination temperature
3. Ms: martensitic range or R phase transformation starting temperature
4. Mf: martensitic transformation termination temperature

[Designation of Document] Drawings

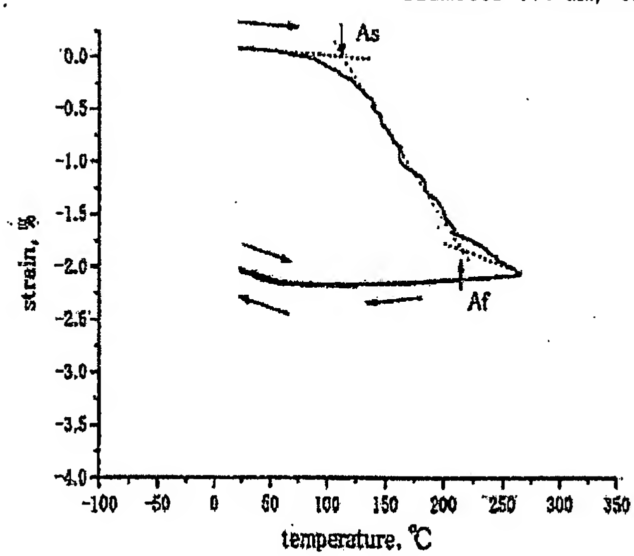
[Fig. 1]

Diameter 0.05 mm, CW 35%



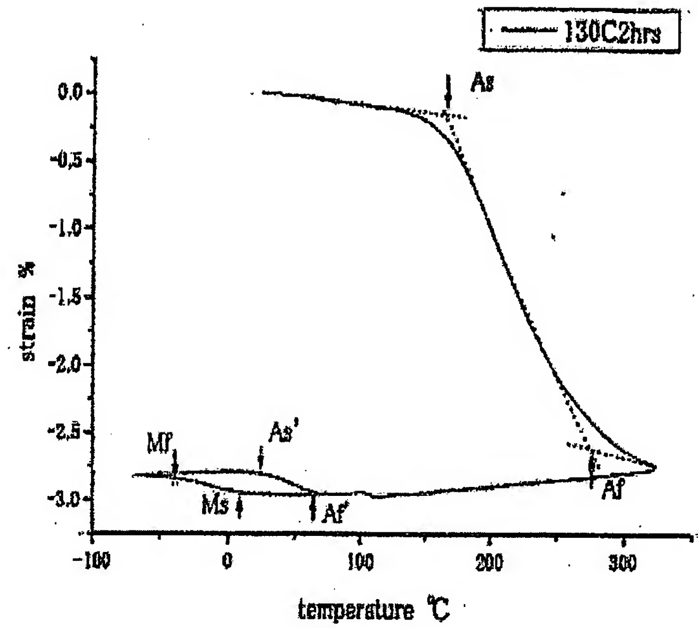
(a)

Diameter 0.4 mm, CW 35%



(b)

[Fig. 2]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As'
Mf
Ms
Af'
Af
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0
100
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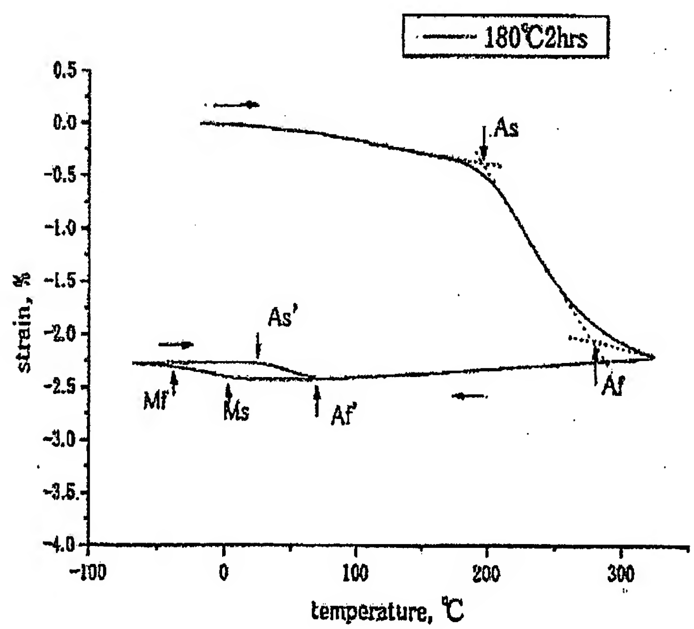
temperature ℃

[Fig. 3]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Mf
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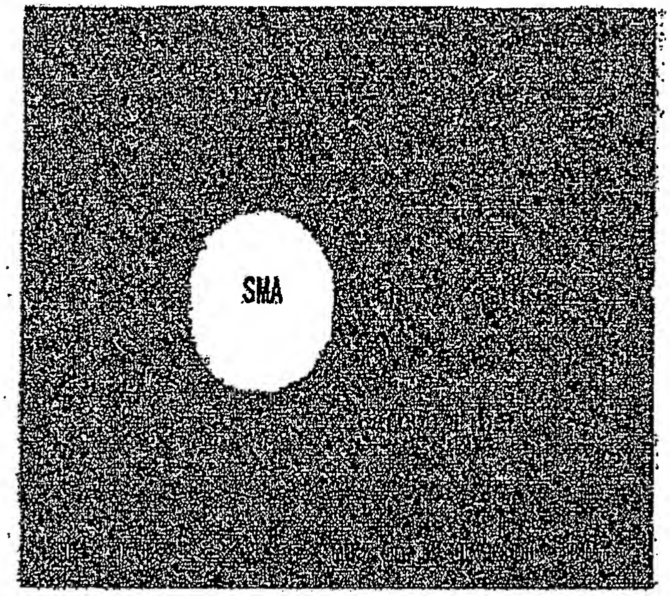
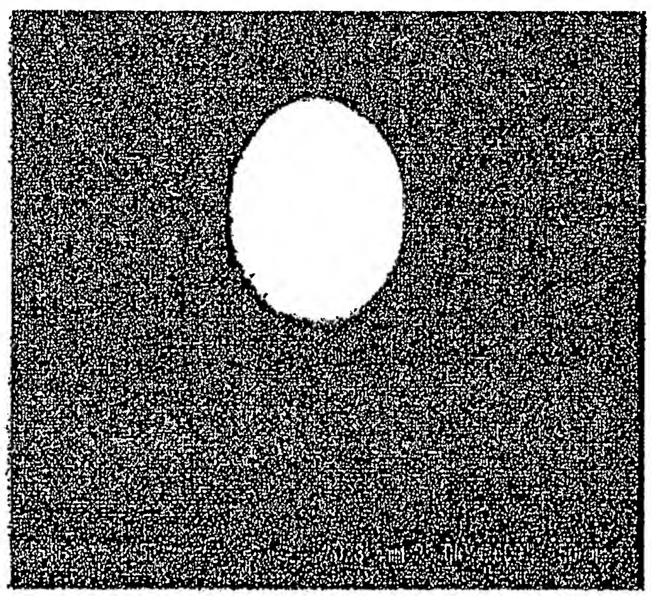
temperature, ℃

[Fig. 4]

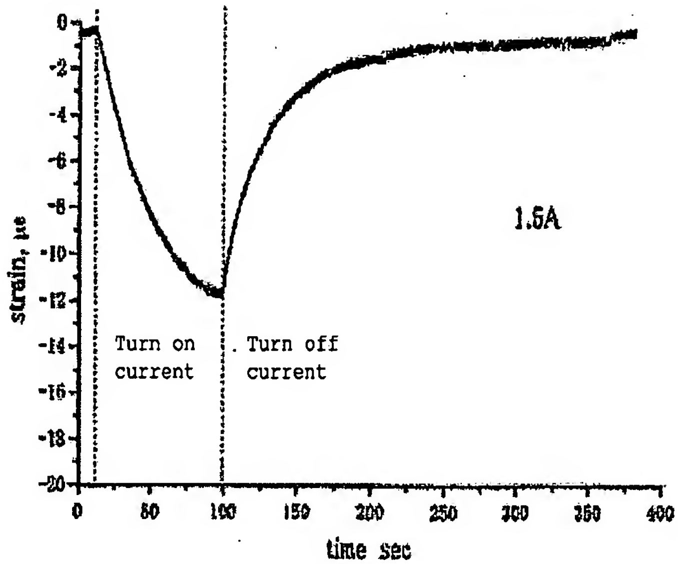


(a)



(b)

[Fig. 5]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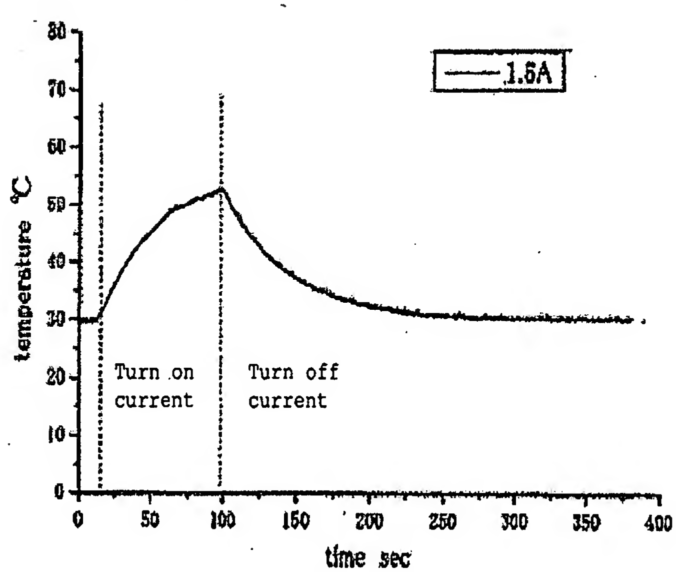
time sec

(a)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400
time sec

(b)

[Designation of Document] Abstract

[Abstract]

[Problem] To provides a functional composite material using an extremely fine shape memory alloy able to retain a pre-strain of 2% or more of a TiNi wire during thermal curing at 180°C even when the wire is not fixed at the both ends, and a process for producing the same.

[Means for Solution] It is a functional composite material molded by hardening an extremely fine shape memory alloy wire having a diameter of 0.06 mm or less in a martensitic phase with a resin matrix material, in which the wire is prepared by using a shape memory alloy which assumes an austenitic phase or a martensitic phase through phase transformation temperatures and subjecting to a cold drawing work.

[Selected Drawing] Fig. 1